The Penetration of Wood by Zinc Chloride.

By Edward G. Mahin.

During the last fifteen years the supply of all kinds of sawed lumber has rapidly diminished. The consequent rise in prices has stimulated the use of methods for prolonging the life of structural timbers that are exposed to excessive weather conditions. Treatment of such timbers to prevent decay has been practically limited, in a commercial sense, to impregnation of the wood with creosote oils or with antiseptic salt solutions, the salt most extensively used being zinc chloride. Against the use of creosote oils two objections have been urged, these being the somewhat excessive cost of the preserving material and the tendency of the lighter fractions of the oils to evaporate under the influence of wind and sun.

While the cost of the zinc chloride would not prohibit its use, it has been noticed for a long time that exposure for a term of years seemed to cause a loss of the efficiency of the preservative. This was long thought to be due to the fact that from moist wood the zinc chloride was gradually lost through a process of outward diffusion similar to that causing "efflorescence" of salts on brick walls. This theory was apparently confirmed by the fact that analysis of old treated wood showed the presence of little zinc chloride in the interior of the piece. In order to remove this objection a process[1] was devised abroad and in 1908 was patented in the United States, for treating wood with zinc chloride, with the addition of aluminium sulphate. It was thought at the time and was originally claimed by the patentees that this process resulted in a fixation of the zinc salt within the wood fibers in such a manner as to practically prevent the outward diffusion and consequent loss of the preservative. It was their theory that some sort of compound was produced between the cellulose of the wood cells and the aluminium sulphate, this compound resulting in a retaining action upon the zinc chloride. The action was likened to the imperfectly understood action of aluminium salts when used as mordants in dyeing. Experiments with washing treated sawdust did not confirm this theory but later unpublished investigations showed that solutions of zinc chloride containing aluminium sulphate, under the same conditions of treatment, penetrated wood ties farther than did solutions of zinc chloride alone, the zinc salt having the same concentration in the two solutions.

[1] The Bruning-Marmetschke process. U. S. patent No. 898,246.

It is a well known fact that zinc chloride in solution hydrolyzes to a considerable extent so that zinc hydroxide or basic zinc chloride precipitates, often in large quantities. The addition of a strong acid redissolves the precipitate, as does also the addition of aluminium sulphate. This solvent action of aluminium sulphate is, without doubt, due to the fact that it also hydrolyzes readily in solution, the resulting sulphuric acid thereby acting to repress the hydrolysis of the zinc chloride. The concentrations of the two salts used in the new process are zinc chloride 3%, aluminium sulphate 1.5%. Such a solution is usually clear, so far as any visible precipitate is concerned. Aluminium sulphate is thus seen to be of use in preventing the precipitation and consequent loss of zinc chloride in the impregnating solution, but there remains unexplained the reason why two *clear* solutions, containing the same concentration of zinc, should penetrate the wood substance to different depths, the solution of the two salts apparently always going farther than the solution of the single salt. It was in order to find, if possible, an explanation of this difference in penetrating power, that the experiments later described were undertaken.

The colloidal character of both zinc hydroxide and aluminium hydroxide is well known. It seemed likely at the outset that even in clear solutions of zinc or aluminium salts there must exist products of hydrolysis in a colloidal condition, consisting of sols of basic salts or even of the hydroxides themselves. If this were the case, since the hydrolysis of zinc chloride is repressed by the presence of the sulphuric acid formed by the hydrolysis of aluminium sulphate, the clear solution of the composite solution should contain less colloidal and more crystalloidal zinc salt than the single solution. The cellulose composing the wood cells is a vegetable colloid and it is not possible for other colloids to diffuse through it. In other words, the wood cells will act as membranes in carrying on a process of dialysis, retaining colloidal material and allowing crystalloidal material to pass. If the solutions possess the difference in character as above described it is easy to see that a difference in penetrating power must follow. The following experiments were undertaken to determine whether zinc chloride solutions in water contain more crystalloidal zinc when aluminium sulphate is present than when it is not present.

Experimental.

Two solutions were prepared, each containing exactly 3% of zinc chloride. To one of these aluminum sulphate was added to the amount of 1.5%.

In making the solutions a quantity of zinc chloride was weighed out and dissolved in such an amount of water as to make a solution somewhat stronger than 3%. Some precipitate was formed and this was filtered out, the remaining clear solution being then standardized and diluted to the required strength. Colloidal membranes were prepared by coating vegetable parchment, of as uniform thickness as possible, with collodion. These were fastened on the ends of tubes having a diameter of about five centimeters, the tubes being of equal cross-section. Of the respective solutions 50 cc. were placed in separate tubes and the latter were immersed in separate beakers of distilled water, adjustment being made so that the water outside was at the same level as the solutions inside. No attempt was made to keep the temperature constant but changes in temperature affected the tubes alike. After certain periods of time, as stated in the tables below, the beakers containing the water and the diffused zinc salt were removed and substituted by beakers containing fresh water. The zinc which had diffused through the membranes was determined by titration with standard solution of potassium ferrocyanide, uranium nitrate being used as indicator. The amount of water placed outside the membranes was, in every case, 100 cc. The standard solution of potassium ferrocyanide was of such concentration that 1 cc. was equivalent to 0.00455 gram of zinc.

In order to correct for any possible difference in thickness or permeability of the two membranes the solutions were interchanged after 234 hours, each solution thereafter diffusing through the membrane that had previously held the other.

In the tables the symbols have the following significance:

B. M. = solution of zinc chloride 3% and aluminum sulphate 1.5%.

B. P. = solution of zinc chloride 3%,

t = hours for each period of diffusion,

T = total hours before reversal of membranes,

T_r = total hours after reversal of membranes,

m = milligrams zinc chloride diffused each period, B. M.,

M = total milligrams zinc chloride diffused, B. M.,

M_r = total milligrams diffused after reversal, B. M.,

p = milligrams zinc chloride, diffused each period, B. P.,

P = total milligrams diffused, B. P.,

P_r = total milligrams diffused after reversal, B. P.,

C_m = milligrams zinc chloride left in B. M. = 1500 — M,

C_p = milligrams zinc chloride left in B. P. = 1500 — P.

TABLE SHOWING RESULTS OF DIALYSIS.

t	T	Tr	m	M	Mr	p	P	Pr	m/p	p/m	Cm	Cp	m.Cp / p.Cm	p.Cm / m.Cp
18	18	...	12.74	12.74	.....	5.00	5.00	..	2.55	....	1487	1495	2.56	....
24	42	...	9.10	21.84	.....	3.64	8.64	...	2.50	....	1478	1491	2.52	....
24	66	...	20.93	42.77	.....	5.91	14.55	.....	3.54	....	1457	1485	3.61	....
27	93	...	29.57	72.34	.....	14.11	28.66	.....	2.09	....	1528	1471	2.22	....
24	117	...	24.57	96.91	.....	15.47	44.13	.....	(1.59)	....	1403	1456	(1.65)	....
24	141	...	35.21	130.12	.....	13.19	57.32	.....	2.52	....	1370	1443	2.65	....
20	161	...	26.85	156.97	.....	11.83	69.15	.....	2.27	....	1343	1431	2.42	....
24	185	...	34.12	191.09	.....	14.10	83.25	.....	2.42	....	1309	1417	2.62	....
24	209	...	31.85	222.94	.....	14.10	97.35	.....	(1.61)	....	1277	1403	(1.76)	....
25	234	...	35.95	258.89	.....	15.02	112.37	.....	2.39	....	1241	1388	2.76	....
23	...	23	15.47	274.36	15.47	31.39	143.76	31.39	.....	2.03	1226	1356	.....	1.83
34	...	57	19.11	293.47	34.58	25.93	169.69	57.32	.....	1.36	1207	1330	.....	1.23
18	...	75	12.74	306.21	47.32	19.11	188.80	76.43	.....	1.50	1194	1311	.....	1.37
25	...	100	15.01	321.22	62.33	18.65	207.45	95.08	.....	1.24	1179	1293	.....	1.13
21	...	121	12.74	333.96	75.07	17.75	225.20	112.83	.....	1.39	1166	1275	.....	1.27
24	...	145	12.29	346.25	87.36	24.57	249.77	137.40	.....	2.00	1154	1250	.....	1.85
48	...	193	11.83	358.08	99.19	20.47	270.24	157.87	.....	1.73	1142	1230	.....	1.61
32	...	225	15.47	373.55	114.66	31.39	301.63	189.26	.....	2.03	1126	1198	.....	1.91

$$\text{Average } \frac{m.C_p}{p.C_m} = 2.45,$$

$$\text{Average } \frac{p.C_m}{m.C_p} = 1.52$$

The average relative rates of diffusion of the zinc in the two solutions will depend upon two conditions: (a) the relative permeability of the membranes and (b) the relative concentrations of zinc salt. If the relative concentrations should undergo no change, through the more rapid diffusion of one solution, the reversal of membranes should change the rates of diffusion so that the value of m/p before reversal should exactly equal the value of p/m after reversal. An inspection of the table shows that the membrane in which B. M. was enclosed before reversal was thinner or less dense, or, from some other reason, more permeable than the other, so that more rapid diffusion took place through this membrane and the solution so enclosed was more rapidly diluted than the other. In order to correct for the resultant change in concentrations the relative rates of diffusion, m/p and p/m, were divided by the relative concentrations, C_m/C_p and C_p/C_m the resultant corrected values being tabluated as $\frac{m.\ C_p}{p.\ C_m}$ and $\frac{p.\ C_m}{m.\ C_p}$. Since the actual concentration of zinc was the same in the two original solutions, the average corrected ratios should be equal unless the zinc were partly in the colloidal, and hence non-diffusible, condition and this to a different extent in the two solutions. The table shows that the average corrected ratio of diffusion of B. M. to B. P. before reversal was 2.45 while the average corrected ratio of diffusion of B. P. to B. M. after reversal was 1.52. The actual concentration of diffusible zinc was therefore greater in the B. M. solution. This actual concentration of diffusible, crystalloidal zinc will be called the "effective concentration."

Let Me = effective concentration of zinc in B. M.,

Pe = effective concentration of zinc in B. P.,

T = thickness (or density) of membrane first containing B. M.,

T′ = thickness of membrane first containing B. P.,

Dm = average rate of diffusion of B. M. before reversal,

Dp = average rate of diffusion of B. P. before reversal,

Dm′ = average rate of diffusion of B. M. after reversal,

Dp′ = average rate of diffusion of B. P. after reversal,

k = a constant, depending upon the temperature;

also let $a = Dm/Dp = 2.45$ and

$b = Dp'/Dm' = 1.52$.

Using these symbols,

$Me = kDmT = kDm'T'$,

$Pe = kDp'T' = kDp'T$;

$Dm = Me/kT$, $Dp = Pe/kT'$, $Dm' = Me/kT'$, $Dp' = Pe/kT$; therefore

$a = MeT'/PeT$ and $b = PeT'/MeT$,

$a/b = Me/Pe$,

$Me/Pe = a/b$.

Substituting the values of a and b as given above, $Me/Pe = 2.45/1.52 = 1.27$.

This ratio of effective concentrations confirms the hypothesis that even clear solutions of zinc chloride contain colloidal products of hydrolysis. Aluminum sulphate, through its own hydrolysis and the formation of free sulphuric acid, causes a partial repression of the hydrolysis of zinc chloride and in 3% zinc chloride solutions, such as are used in wood preserving, there is approximately 80% as much zinc present in true solution as is the case when 1.5% of aluminum sulphate has been added. The remaining zinc is in the form of a hydrosol of basis zinc chloride or of zinc hydroxide and cannot pass into the interior of treated wood but must be left in the outer layers. It is to be expected that any other easily hydrolyzed salt of a strong acid would have a similar effect upon the penetration of zinc salts into wood. The use of free acid itself would have the same effect if it were used intelligently.

Further experiments are now in progress.

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